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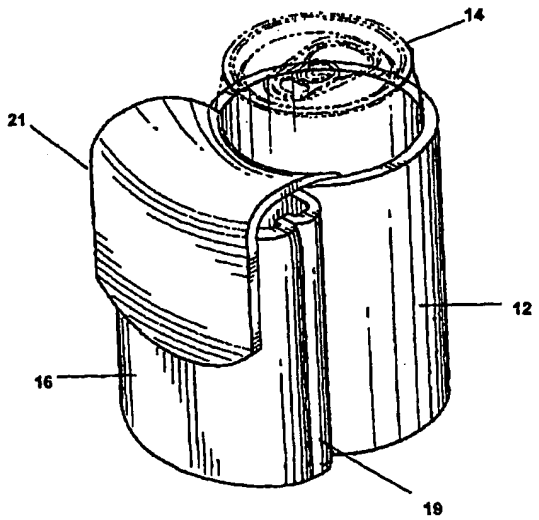
(54) Title: FLEXIBLE FOAM PRODUCTS INCORPORATING AN INORGANIC ANTIMICROBIAL AGENT AND METHODS OF MANUFACTURE



(57) Abstract: Flexible expanded plastic cellular foam having a surface containing an inorganic antimicrobial agent and methods of manufacture of products of such foam has at least one surface that is to be in contact with the user's hand and such surface contains the inorganic antimicrobial agent. The agent, which can be antimicrobial ceramic particles, e.g., zeolite, is present in the surface in an effective amount to kill or retard growth of bacteria. The agent can be placed on a surface of the mold to be formed as part of the surface as the foam expands, or be contained in a coating applied to the surface.

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FLEXIBLE FOAM PRODUCTS INCORPORATING AN INORGANIC ANTIMICROBIAL AGENT AND METHODS OF MANUFACTURE

Field of the Invention

The present invention relates to flexible foam products incorporating an inorganic antimicrobial agent and methods of manufacture.

Background of the Invention

Flexible, polymeric foam and products made therefrom are well known. The foam is usually of polyurethane polymer formed by reacting with an organic prepolymer of the polyurethane containing polyisocyanate with an isocyanate reactive component. The reaction causes an expansion of the polymer into a cellular foam. An example of this is disclosed in U.S. Patent No. 5,314,928. The resulting foam is often formed in flat sheet form or the foam forming materials are injected into a mold to form a desired shape upon expansion. Basically, the foam is somewhat soft and can be depressed, and it is flexible.

Such foams are used in a variety of products. Because of the heat insulating properties it has been formed as a holder into which a hot or cold beverage container is inserted, such as shown in U.S. Patent No. 5,857,601 and Des. 399,707. The user holds the outer surface of the holder so the hand does not transmit heat to cold beverage, or so that heat from a hot beverage does not burn the user's hand. To make such a holder, a piece of sheet foam is folded and its ends joined to form a cylinder. The holder also can be molded with a hard outer skin formed by a urethane type "paint" placed on the surface of a mold used. Often, an advertising symbol or message is printed on the holder outer surface. The flexible foam is also used as packaging material.

U.S. Patent No. 4,937,273, to Marcus, describes an antibacterial flexible polyurethane foam comprising an inorganic antibacterial agent, such as silver zeolite. The agent

is added to the foaming mixture during production of the polyurethane foam, and is present throughout the resulting foam.

For a number of applications, it would be desirable to provide the surface of the foam which is to be contacted by a user or by an object that is held with antimicrobial properties. For example, in a beverage holder, some of the container contents may spill over to the holder where it provides a site for bacterial growth that can be contacted by the user's hand. The same is possible for packaging material which can become contaminated and thus transfer bacteria to the person who touches the foam.

There are a number of advantages associated with foam products containing antimicrobial particles only on the surface of the product which will be contacted by the hand of the user, and as opposed to particles throughout the foam. For example, there are economic advantages associated with the use of less antimicrobial zeolite particles.

There are advantages associated with foams containing an antimicrobial inorganic agent in which the agent is not present in the foaming mixture during production of the foam, and is instead added during a post-foaming step. The presence of the antimicrobial particles in the foaming mixture may influence the foaming process, and requires adjustments to the various parameters used during foaming.

Accordingly, it would be desirable to provide the flexible foam with antimicrobial properties in order to prevent or retard bacterial growth.

Summary of the Invention

The present invention provides a flexible foam that has inorganic antimicrobial properties. In accordance with the invention, the foam can be made with an inorganic antimicrobial agent incorporated into the foam resin component so that it is present on the surfaces of the foam, including surfaces which can be contacted by the hand of a user. The agent also can be provided as a coating applied to selected areas of the foam product, such as by

a separate application or by incorporating it into the molding process as a "paint" applied to the mold to form a skin on the product surface, as described in the aforesaid U.S. Patent 4,209,564. The agent preferably comprises antimicrobial ceramic particles, e.g., ion-exchanged zeolites containing antimicrobial metal ions.

In particular embodiments, the inorganic antimicrobial agent may be present only on the surface of the foam, and is not present in the interior of the foam. In these embodiments, the inorganic antimicrobial agent is generally not included in the foaming mixture, but is added during a post-foaming step. For example, the antimicrobial agent may be sprayed into the mold that is used to form the foam, or may be coated onto the finished foam structure.

Objects of the Invention

It is therefore an object of the invention to provide flexible cellular foam and products made therefrom having at least a surface that includes an inorganic antimicrobial agent.

Still a further object is to provide a method of manufacturing flexible cellular foam products having antimicrobial properties.

A further object is to provide a flexible foam product, such as a beverage holder, in which the outer and/or the inner surface incorporates an inorganic antimicrobial agent.

It is also an object of the invention to provide a flexible foam product containing an inorganic antimicrobial, in which the antimicrobial agent is not added to the foaming mixture, but is added during a post-foaming step.

Brief Description of the Drawings

Other objects and advantages of the present invention will become more apparent upon reference to the following specification and annexed drawing in which:

Fig. 1 is a perspective view of a beverage can holder made in accordance with the invention to incorporate the antimicrobial agent.

Detailed Description of the Invention

Referring to Fig. 1, this shows a beverage holder 10 made of flexible plastic foam. It includes a sleeve of generally cylindrical form, shown for holding a cold beverage can 14. The sleeve 12 is of any desired size and thickness. The sleeve also can be molded with the bottom (not shown). It also can be a flat piece of the foam that is rolled into a cylindrical shape and the opposing ends of the piece are joined together. A bottom piece of foam is attached to the cylinder, such as by an adhesive. The holder, which is shown in greater detail in U.S. Patent Des. 399,707, also has an auxiliary insulator 16 which is formed by taking a flat sheet piece of the flexible foam, folding it and joining it, such as by a suitable adhesive, along a seam 19. The auxiliary insulator 16 is attached to the sleeve 12, also such as by an adhesive, to provide additional insulating. The holder also has a flap 21 formed from a piece of the foam, or some other material, with one end fastened to the interior of the sleeve and which can be folded over to protect the top of the can, such as when it is open.

The holder 10 is only illustrative of the types of products that can be made of expanded foam. Here, two general components are shown. One is the sleeve 12 which is preferably molded, and the other being the auxiliary insulator 16 which is a piece of the flat flexible foam. The foam forming the holder is of any suitable type made by consistent processes with a material such as polyurethane to obtain the desired degree of flexibility. In accordance with the invention one or both of the surfaces of sleeve 12 and sometimes at least the outer surface of the insulator 16 is provided with an antimicrobial agent. The purpose of the agent is to kill or reduce the growth of bacteria and prevent the limitation of bacteria growth sites.

In the manufacture of conventional flexible foam products, such as of polyurethane as described in the patents above, the foam constituents, such as polyisocyanate and a polyol, are brought together in a mixing head and then injected or sprayed into the cavity of a suitable mold. The constituents expand in the mold to form the final product. After cooling, the finished product is removed from the mold. To make sheets of the flexible foam material, such as for insulator 16, the components are reacted on a moving belt, in molds, by extrusion or other suitable conventional techniques. Various techniques and material compositions, such as described in U.S. Patent No. 5,141,684, can be used to make the inner and outer surfaces of the foam of higher density so as to be able to reduce wear. Although these patents describe a rigid foam, the idea can be extended to flexible foam.

In the process for making an object such as the sleeve 12 with a bottom, a mold of two parts is used that forms a cavity which defines the general shape of the sleeve. The composition for forming the foam is sprayed or injected into the mold cavity. All of the equipment and processing for forming expanded foam products are well known.

In accordance with the invention, at least and preferably only the outer surface of the sleeve by which the user grasps the holder, is to contain the inorganic antimicrobial agent. This protects the user's hand from becoming contaminated by bacteria growing on the outer surface. The outer surface of the insulator 16 can also be provided with the agent. Since the outer surface of the sleeve and also of the insulator, if desired, contains the antimicrobial agent, the desired action of killing bacteria or reducing its growth rate is accomplished.

The following describes processes by which the agent can be incorporated into or onto the surface of the flexible cellular foam.

Incorporating the agent in the resin - the antimicrobial agent can be directly incorporated into the resin that is used as one of the components of the expanded foam, for example, liquid polyurethane. A preferred antimicrobial agent is an antibiotic zeolite and particularly zeolites incorporated as ceramic particles and those which contain silver. Suitable

zeolites and a method for incorporating them into the resin are disclosed in U.S. Patent Nos. 4,938,955 and 4,906,464. The resins for the foam can be those such as polyurethane, which is usually preferred, as well as, polyethylene, polypropylene, polystyrene, polyvinyl chloride, and others as disclosed in said patents.

In a typical process for forming the polymer resin constituent of the foaming material used to make the sleeve, a zeolite is used as the antimicrobial agent. Zeolites are often obtained in master batches of pellets of low density polyurethane, polyethylene, polypropylene, polyurethane and polystyrene, the pellets containing up to about 20 wt% of the zeolite. Thus, the zeolites in plastic pellet form can be easily mixed with the resin used as the thermoplastic material, e.g., polyurethane resin used to make the foam. Typically, where the resin is in liquid form, such as polyurethane, the master batch polyurethane pellets are ground to desired size and added to the polyurethane liquid. Alternatively, the ceramic zeolite particles can be added directly to the liquid resin. Other antimicrobial agents, as described below, are also suitable and would be processed in a manner consistent with the agent and resin used.

The foam constituents, including the resin with the zeolite particles, are used in the normal manner, such as being injected into a mold. Upon the expansion taking place, the particles of the agent are present throughout the surfaces of the cells forming the foam product. The agent is present on both the inner and outer surfaces of the sleeve 12. For example, when resin containing the particles of the agent is used to make a flat foam sheet, the agent particles also are present on the inner and outer surface. An insulator 16 made from such a flat sheet would have the agent present at only its inner and outer surfaces.

The antimicrobial particles are preferably present in a concentration by weight in the resin in an effective amount. This means that there is a sufficient amount of the antimicrobial agent added to or combined with other materials, such as the plastic resin, such as to be present on the desired surface or surfaces, to prevent or inhibit the growth of bacterial and/or fungal organisms or to kill such organisms. The amount of the agent will vary based on

the specific agent used and the material with which it is mixed or added to and upon known factors such as type and use of the flexible foam product. Environmental factors such as the temperature of the sleeve also should be taken into consideration. It is within the ability of one skilled in the art to relatively easily determine an effective amount of the antimicrobial agent to be used with each material.

Typical ranges of the basic zeolite agent in the resin constituent of the foam have been found to be of from 0.01 to 10.0wt%, more preferably from 0.01 to 8.0wt%, and most preferably from 0.1 to 5.0wt%.

A preferred embodiment of the sleeve according to the invention has:

resin	polyurethane and compatible foaming agent
antimicrobial agent	AJ10D (Shinigawa)
wt% of agent in resin	2.0%
particle size of agent	1.0 micron

Placing Agent on the Mold - in this process, the agent is not present in the foaming mixture, but is applied to the portion of the mold forming the surface that is desired to contain the agent. There are several ways to do this.

First, the basic zeolite ceramic particles, or pellets ground to suitable size, e.g. up to 3mm across containing the particles, can be mixed in the "paint" material as described in the aforesaid U.S. Patent No. 4,209,564. After the molding process takes place a skin is formed on the outer surface of the sleeve. In a preferred embodiment using this process:

agent particles	AJ10D (Shinigawa) zeolite
size of particles	1.0 micron
wt. % of agent in the paint	5% by weight of the master batch

In a second technique, plastic pellets of desired size containing the particles of the agent are adhered to the appropriate mold surface, such as by an acrylic. The foam composition is inserted into the mold cavity and expands against the mold surfaces. During expansion of the foam the particles of the agent, or the pellets, containing the particular agent,

on the mold portion that forms the sleeve 12 outer surface and inner surface if desired, become embedded in such surface and are available for antimicrobial action as described above.

Coating the Surface - in this embodiment the sleeve 12 or sheet of flexible foam is formed in the normal manner. After its formation, the desired surface, or part thereof, has a coating applied which contains the agent.

For the sleeve 12, the coating is adhered to the outer surface. Polymer coatings are preferred for this embodiment. It also can be applied to any surface or part thereof of the insulating member. The polymers can be of silicon rubber and hydrophilic polymers. The coating preferably can be of, for example, a hydrophilic polymer such as hydrophilic polyurethane. The antimicrobial agent comprises particles which are mixed with the coating material.

The coating with the agent is applied to the desired surface by any suitable technique, such as spraying or painting. The agent is available where applied on the surface to perform its antimicrobial action.

The agent comprises by weight of the coating material of between about from 0.1% - 100 wt%, more preferably from between about 0.1% to 75.0%, and most preferably from 0.6 to 50.0%. As explained above, an effective amount of the agent is used.

A typical embodiment of the coating is:

coating material	acrylic
agent	AJ10D (Shinigawa)
agent particle size	1.0 micron
wt% of agent in coating	5.0%

As to the inorganic antimicrobial agent incorporated in the resin or used in the coating, a number of metal ions, which are inorganic materials, have mercury, tin, lead, bismuth, cadmium, chromium and thallium ions. These antimicrobial metal ions (cations) are believed to

exert their effects by disrupting respiration and electron transport systems upon absorption into bacterial or fungal cells. Antimicrobial metal ions of silver, gold, copper and zinc, in particular, are considered safe even for *in vivo* use. Antimicrobial silver ions are particularly useful for *in vivo* use due to the fact that they are not substantially absorbed into the body. That is, if such materials are used they should pose no hazard.

In one embodiment of the invention, the inorganic antimicrobial metal containing composition is an antibiotic metal salt. Such salts include silver acetate, silver benzoate, silver carbonate, silver ionate, silver iodide, silver lactate, silver laureate, silver nitrate, silver oxide, silver palpitate, silver protein, and silver sulfadiazine. Silver nitrate is preferred. These salts are particularly quick acting, as no release from ceramic particles is necessary to function antimicrobially.

Antimicrobial or antibiotic ceramic particles useful with the present invention include zeolites, hydroxy apatite, zirconium phosphates or other ion-exchange ceramics. Zeolites are preferred, and are described in the preferred embodiments of the invention.

Hydroxy apatite particles containing antimicrobial metals are described, e.g., in U.S. Patent No. 5,009,898. Zirconium phosphates containing antimicrobial metals are described, e.g., in U.S. Patent Nos. 5,296,238; 5,441,717; and 5,405,644. Inorganic particles such as the oxides of titanium, aluminum, zinc and copper may be coated with a composition which confers antimicrobial properties, for example, by releasing antimicrobial metal ions such as silver ions, e.g., in U.S. Patent No. 5,180,585. Inorganic soluble glass particles containing antimicrobial metal ions, such as silver, for example, are described, e.g., in U.S. Patent Nos. 5,766,611 and 5,290,544.

Antibiotic or antimicrobial zeolites are preferred. These have been prepared by replacing all or part of the ion-exchangeable ions in zeolite with ammonium ions and antimicrobial metal ions, as described in U.S. Patent Nos. 4,938,958 and 4,911,898. Such zeolites have been incorporated in antimicrobial or antibiotic resins (as shown in U.S. Patent

Nos. 4,938,955 and 4,906,464) and polymer articles (U.S. Patent No. 4,775,585). Polymers including the antimicrobial zeolites have been used to make refrigerators, dish washers, rice cookers, plastic film vacuum bottles, plastic pails, and garbage containers. Other materials in which antimicrobial zeolites have been incorporated include flooring, wall paper, cloth, paint, napkins, plastic automobile parts, catheters, bicycles, pens, toys, sand, and concrete. Examples of such uses are described in US Patents 5,714,445; 5,697,203; 5,562,872; 5,180,585; 5,714,430; and 5,102,401. Zeolite ceramic particles have been shown to possess antimicrobial or antibiotic activity, including those containing antimicrobial silver, copper or zinc ions (cations). These applications involve slow release of antimicrobial silver from the zeolite particles. This is suitable for the surfaces of the flexible cellular foam.

Antimicrobial or antibiotic zeolites are well-known and can be prepared for use in the present invention using known methods. These include the antimicrobial zeolites disclosed, for example, in U.S. Patent Nos. 4,938,958 and 4,911,898.

Either natural zeolites or synthetic zeolites can be used to make the antibiotic zeolites used in the present invention. "Zeolite" is an aluminosilicate having a three dimensional skeletal structure that is represented by the formula: $XM_{2/n}$-O-Al_2O_3-$YSiO_2ZH_2O$. M represents an ion-exchangeable ion, generally a monovalent or divalent metal ion, n represents the atomic valency of the (metal) ion, X and Y represent coefficients of metal oxide and silica respectively, and Z represents the number of waters of crystallization. Examples of such zeolites include A-type zeolites, X-type zeolites, Y-type zeolites, T-type zeolites, high-silica zeolites, sodalite, mordenite, analcite, clinoptilolite, chabazite and erionite. The present invention is not restricted to use of these specific zeolites.

The ion-exchange capacities of these zeolites are as follows: A-type zeolite = 7 meq/g; X-type zeolite = 6.4 meq/g; Y-type zeolite = 5 meq/g; T-type zeolite = 3.4 meq/g; sodalite = 11.5 meq/g; mordenite = 2.6 meq/g; analcite = 5 meq/g; clinoptilolite = 2.6 meq/g;

chabazite = 5 meq/g; and erionite = 3.8 meq/g. These ion-exchange capacities are sufficient for the zeolites to undergo ion-exchange with ammonium and antimicrobial metal ions.

The specific surface area of preferred zeolite particles is preferably at least 150 m^2/g (anhydrous zeolite as standard) and the SiO_2/Al_2O_3 mol ratio in the zeolite composition is preferably less than 14, more preferably less than 11.

The antimicrobial or antibiotic metal ions used in the antibiotic zeolites should be retained on the zeolite particles through an ion-exchange reaction. Antimicrobial metal ions which are adsorbed or attached without an ion-exchange reaction exhibit a decreased bactericidal effect and their antimicrobial effect is not long-lasting. Nevertheless, it is advantageous for imparting quick antimicrobial action to maintain a sufficient amount of surface adsorbed metal ion.

In the ion-exchange process, the antimicrobial metal ions tend to be converted into their oxides, hydroxides, basic salts etc. either in the microforms or on the surfaces of the zeolite and also tend to deposit there, particularly when the concentration of metal ions in the vicinity of the zeolite surface is high. Such deposition tends to adversely affect the bactericidal properties of ion-exchanged zeolite.

In an embodiment of the antimicrobial or antibiotic zeolite, a relatively low degree of ion exchange is employed to obtain superior bactericidal properties. It is believed to be required that at least a portion of the zeolite particles retain metal ions having bactericidal properties at ion-exchangeable sites of the zeolite in an amount less than the ion-exchange saturation capacity of the zeolite. In one embodiment, the zeolite employed in the present invention retains antimicrobial metal ions in an amount up to 41% of the theoretical ion-exchange capacity of the zeolite. Such ion-exchanged zeolite with a relatively low degree of ion-exchange may be prepared by performing ion-exchange using a metal ion solution having a low concentration as compared with solutions conventionally used for ion exchange.

The zeolite preferably comprises an integral discoloration agent such as ion-exchanged ammonium. Although ammonium ions may be contained in the zeolite at a concentration as high as about 20% by weight of the zeolite, it is desirable to limit the content of ammonium ions to about 0.5 to about 2.5%, more preferably from about 0.5 to about 2.0%, and most preferably, from about 0.5 to about 1.5% by weight of the zeolite.

In the antimicrobial zeolite particles used in the present invention, ion-exchangeable ions (cations) present in zeolite, such as sodium ions, calcium ions, potassium ions and iron ions are partially replaced with antimicrobial metal ions, such as silver. The antimicrobial zeolite typically comprises from about 0.5 to about 15% and preferably from about 0.5 to about 2% by weight of ion-exchanged silver based upon 100% total weight of zeolite. Other antimicrobial metal ions may be included in the zeolite such as copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, thallium, or a combination thereof. Such ions may co-exist in the antimicrobial zeolite particles since they do not prevent the bacterial effect of the zeolite particles. These antimicrobial metal ions may be incorporated into the zeolite by themselves or in a mixture. In one embodiment, the zeolite contains from about 0.1 to about 15% by weight of silver ions and from about 0.1 to about 8% by weight of copper or zinc ions.

The antimicrobial metal ion is preferably present in the range of from about 0.1 to 20wt.% of the zeolite. In one embodiment, the zeolite contain from 0.1 to 20wt.% of silver ions and from 0.1 to 20wt.% of copper or zinc ions. Although ammonium ion can be contained in the zeolite at a concentration of about 20 wt.% or less of the zeolite, it is desirable to limit the content of ammonium ions to from 0.5 to 15 wt.%, preferably 1.5 to 5 wt.%. Weight% described herein is determined for materials dried at temperatures such as 110□C, 250□C or 550□C as this is the temperature employed for the preferred post-manufacturing drying process.

A preferred antimicrobial zeolite is type A zeolite containing either a combination of ion-exchanged silver, zinc, and ammonium or silver and ammonium. One such zeolite is manufactured by Shinagawa, Inc. under the product number AW-10N and consists of

0.6% by weight of silver ion-exchanged in Type A zeolite particles having a diameter of about 2.5μ. Another formulation, AJ-10N, consists of about 2% by weight silver ion-exchanged in Type A zeolite particles having a diameter of about 2.5μ. Another formulation, AW-80, contains 0.6% by weight of silver ion-exchanged in Type A zeolite particles having a diameter of about 1.0μ. Another formulation, AJ-80N, consists of about 2% by weight silver ion-exchanged in Type A zeolite particles having a diameter of about 1.0μ. These zeolites preferably contain about between 0.5% and 2.5% by weight of ion-exchanged ammonium. A further product is AJ1OD, which consists of about 2% by weight of silver ion exchanged in Type A zeolite particles having a diameter of about 1.0μ.

The zeolite are often obtained in master batches of low density polyethylene, polypropylene, or polystyrene, containing 20wt% of the zeolite. Thus, they can be easily mixed with the resins used as materials for forming the foam.

The antimicrobial properties of the antimicrobial zeolite particles of the invention may be assayed while in aqueous formulations using conventional assay techniques, including for example determining the minimum growth inhibitory concentration or content (MIC) with respect to a variety of bacteria, eumycetes and yeast. In such a test, the bacteria listed below may be employed:

Bacillus cereus varmycoides;
Escherichia coli;
Pseudomonas aeruginosa;
Staphylococcus aureus;
Streptococcus faecalis;
Aspergillus niger;
Aureobasiduim pullulans;
Chaetomium globosum;
Gliocladium virens;
Penicillum funiculosum;
Candida albicans; and
Saccharomyces cerevisiae.

The assay for determining MIC can be carried out by smearing a solution containing bacteria for inoculation onto a plate culture medium to which a test sample of the encapsulated antibiotic zeolite particles is added in a particular concentration, followed by incubation and culturing of the plate. The MIC is defined as a minimum concentration thereof required for inhibiting the growth of each bacteria.

Safety and biocompatibility tests were conducted on the antibiotic zeolite employed in the invention. ISO 10993-1 procedures were employed. The following results were obtained:

Cytotoxicity: **Non-Toxic**
Acute Systemic Toxicity: **Non-Toxic**
Oral Toxicity: Safer than table salt
Intracutaneous Toxicity: **Passed**
Skin Irritation Test: **Non-Irritant**
Chronic Toxicity: **No Observable Effect**
In-vitro Hemolysis: **Non-Hemolytic**
30-day Muscle Implant Test: **Passed**
60-day Muscle Implant Test: **Passed**
90-day Muscle Implant Test: **Passed**
Ames Mutagenicity Test: **Passed**
Pyrogenicity: **Non-Pyrogenic**

Thus, the antimicrobial zeolite are exceptionally suitable under relevant toxicity and biocompatibility standards for use in the flexible foam and products made from it.

Alternative embodiments will be recognized by those skilled in the art and are intended to be included within the scope of the claims. Accordingly, the above description should be construed as illustrating and not limiting the scope of the invention.

WE CLAIM:

1. A flexible plastic cellular foam material having a surface and an interior, wherein said surface of said foam material comprises an inorganic antimicrobial agent, and said interior does not comprise an inorganic antimicrobial agent.

2. The flexible foam of claim 1 wherein said inorganic agent comprises antimicrobial ceramic particles.

3. The flexible foam of claim 2 wherein said ceramic particles are zeolite particles.

4. The flexible foam of claim 2 wherein said zeolite particles contain silver cations as the active ingredient.

5. The flexible foam of claim 1 wherein said agent is present in a coating on said surface.

6. The flexible foam of claim 5 wherein said agent comprises between from 0.6 to 50% by weight of said coating material.

7. The flexible foam of claim 6 wherein said inorganic agent comprises antimicrobial ceramic particles.

8. The flexible foam of claim 7 wherein said ceramic particles are zeolite particles.

9. The flexible foam of claim 8 wherein said zeolite contains silver cations as the active ingredient.

10. A flexible plastic cellular foam comprising an inorganic antimicrobial agent, said foam prepared by forming a composition comprising polyol and polyisocyanate in a mixing head, and injecting or spraying said composition into a mold, wherein said composition does not contain said inorganic antimicrobial agent.

11. The flexible plastic cellular foam of claim 10, wherein said inorganic agent comprises antimicrobial ceramic particles.

12. The flexible plastic cellular foam of claim 11, wherein said ceramic particles are zeolite particles.

13. The flexible plastic cellular foam of claim 12, wherein said zeolite particles contain silver cations as the active agent.

14. A method of forming a product of a flexible plastic cellular foam having at least one surface containing an inorganic antimicrobial agent, said method comprising the steps of:

providing a mold having a cavity of the shape of the product;

injecting a mixture of a resin and expansion agent into said mold for expansion into said product; and

applying said agent to the portion of said mold that shapes said at least one surface which is to contain said agent and wherein said agent becomes embedded into the inner surface as the resin mixture expands and cools;

thereby forming said at least one surface to contain an inorganic antimicrobial agent.

15. The method of claim 14, wherein said inorganic antimicrobial agent comprises antimicrobial ceramic particles.

16. The method of claim 15, wherein said ceramic particles are zeolite particles.

17. The method of claim 12, wherein said zeolite contains silver cations as the active ingredient.

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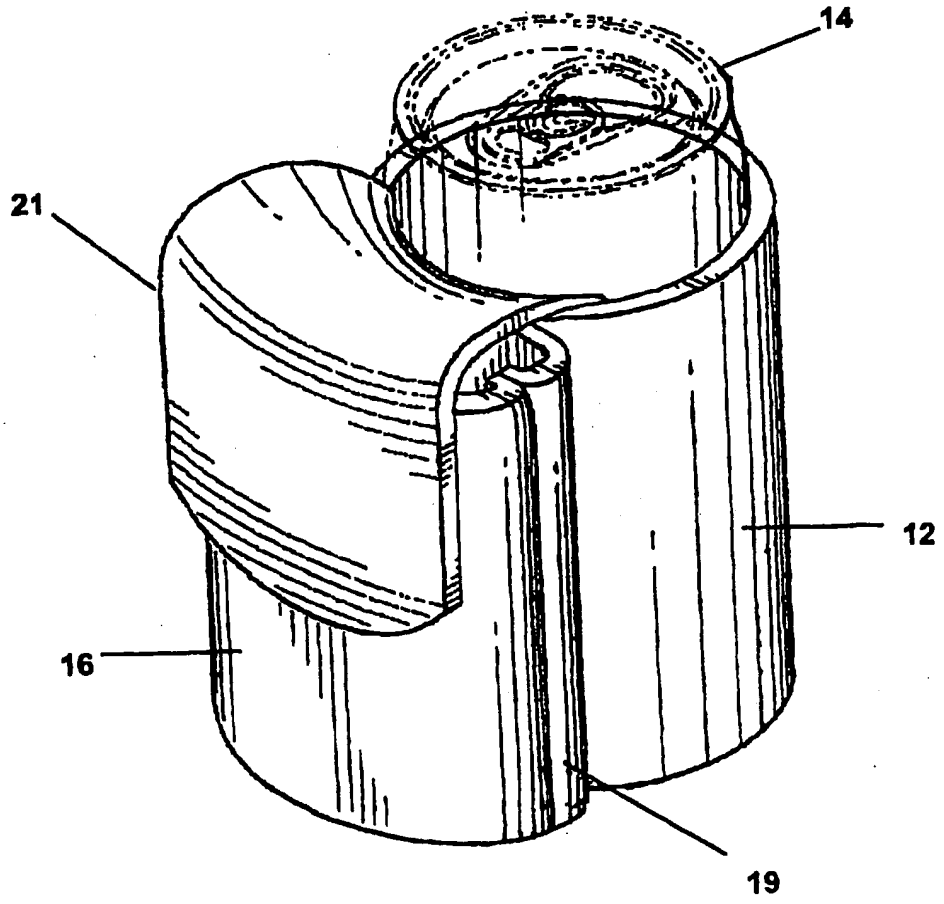

Fig. 1

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7 February 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/34686 A3

(54) Title: FLEXIBLE FOAM PRODUCTS INCORPORATING AN INORGANIC ANTIMICROBIAL AGENT AND METHODS OF MANUFACTURE

(57) Abstract: Flexible expanded plastic cellular foam having a surface containing an inorganic antimicrobial agent and methods of manufacture of products of such foam has at least one surface that is to be in contact with the user's hand and such surface contains the inorganic antimicrobial agent. The agent, which can be antimicrobial ceramic particles, e.g., zeolite, is present in the surface in an effective amount to kill or retard growth of bacteria. The agent can be placed on a surface of the mold to be formed as part of the surface as the foam expands, or be contained in a coating applied to the surface.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 00/42123

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/36 A01N25/34 A01N25/16 C08J9/00 //C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 64259 A (HEALTHSHIELD TECHNOLOGIES L L) 2 November 2000 (2000-11-02) the whole document	1-17
X	DATABASE WPI Section Ch, Week 199734 Derwent Publications Ltd., London, GB; Class A96, AN 1997-369342 XP002168178 & JP 09 157110 A (TOKYO PACKS KK), 17 June 1997 (1997-06-17) abstract	1-3,5-8, 10-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 August 2001	19/09/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Oudot, R

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inte onal Application No
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JP 9157110 A	17-06-1997	NONE	